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TITLE: Continuous process for making melt-processable optical grade ring-opened polycyclic (co) polymers in a single-stage multi-zoned reactor

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CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Continuous process for making melt-processable optical grade ring-opened polycyclic (co)polymers in a single-stage multi-zoned reactor

AB A continuous process for the solution polymerization of appropriate polycycloolefins in a ROMP zone to obtain a processable ROMP homo- or copolymer in solution, and subsequent hydrogenation of the ROMP (co)polymer without removing the residual ROMP catalyst and co-catalyst, provides an optical product having a mol wt M.sub.w in the range from 50,000-300,000 and polydispersity M.sub.w /M.sub.n in the range from 1.3-5.0, more preferably from 1.3-3, the lower the polydispersity the more desirable the physical properties of the (co)polymer. The process comprises, (A) continuously polymerizing a substantially anhydrous solution of said monomer by ring opening metathesis polymerization in at least a first and a last reaction zone of a multi-zoned, single-stage, reaction vessel to form an unsaturated polymer cement essentially free of unreacted monomer; (B) hydrogenating said unsaturated polymer cement in the presence of an effective amount of a nickel-containing hydrogenation catalyst in an amount sufficient to produce a hydrogenareal cement wherein more than 97% of double bonds in said unsaturated polymer are converted to single bonds; (C) removing more than 99% by weight of spent polymerization catalyst, used hydrogenation catalyst and filter aid present in said hydrogenated cement to produce an essentially solids-free hydrogenated cement; (D) devolatilizing said solids-free

hydrogenated cement to produce a thickened hydrogenated polymer cement, and, (E) recovering a solid polymer which meets particle count specifications for optical grade polymer.

SUMM The art of ring-opening metathesis polymerization (referred to as "ROMP") is well known (see, for example, "Encyclopedia of Polymer Science and Engineering", 2nd Ed., H. F. Mark, et al., Ed., John Wiley and Sons, New York, 1987, Vol. 9, pages 634-668), and a variety of polymers have been obtained by this method. For example, U.S. Pat. Nos. 4,069,376, 4,110,528, 4,136,247, 4,136,248, 4,136,249, and 4,178,424, all assigned to the B. F. Goodrich Company, describe such polymers and their methods of preparation.

SUMM During the past decade, many attempts have been made to provide a viable continuous polymerization process to make ring-opened thermoplastic polymers of cyclic and polycyclic olefin monomers with the justifiable expectation that one skilled in the art should be able to do so with the usual trial and error.

SUMM U.S. Pat. No. 5,053,471 to Goto et al describes a polymerization process which states that the two-step process, namely, polymerization and subsequent hydrogenation, may be carried out continuously. Though their disclosure states "Therefore, these two steps can be effected continuously without separating the ring-opening (co)polymer after the ring opening polymerization reaction." (col 14, lines 61-63), the polymer must first be separated from the ROMP catalyst before the polymer is hydrogenated. In example 1 they start with 50 g of monomer and recover 45 g of polymer. In example 10, 20 g of this polymer was dissolved in toluene and hydrogenated with a nickel naphthenate catalyst. To make the separation, a mixture of 'good' and 'poor' solvents which are mutually miscible, is used. To remove the first catalyst, a dilute aqueous organic acid is used, then "the organic layer is, . . . subjected to a conventional polymer recovery step to isolate a polymer freed of the polymerization catalyst." Clearly, the '471 process is not continuous, and the only enabling disclosure specifically teaches that the ROMP catalyst must be removed before the polymer is hydrogenated.

SUMM It has also been discovered that the hydrogenated melt-processable copolymer produced by ring-opening metathesis polymerization in the polyreactor cannot be centrifuged to make the desired separation. Filtration is required in a multiple-step filtration process in which a plate-and-frame filter press is used for the primary and secondary filtration stages. Up to 95% by wt of the gel in the hydrogenated polymer solution, the polymerization and hydrogenation catalysts and filter aid are removed in the primary filter press to produce a primary filtrate; in the secondary filter press a secondary filtrate is produced containing only submicron size particles. Optionally, third and fourth filtration stages may be used, the filtrate from a preceding stage being continuously introduced to the succeeding stage. A third stage using a cartridge filter with a submicron porous filter medium is found to provide excellent optical grade copolymer which meets "particle count" specifications. Because of the processing expense related to the peculiar properties of the solids in the feedstream from the hydrogenation zone require the foregoing combination of filtration steps in any practical scheme to provide the optical grade polymer solution.

SUMM It is therefore a general object of this invention to provide a continuous ROMP process comprising, maintaining a single-stage polymerization in multiple zones including at least a first and a last

reaction zone, wherein the first zone is maintained at a temperature in the range from 70° C-100° C. by mixing a reaction medium consisting essentially of at least one of the aforesaid cycloolefin monomers, a C.sub.3 -C.sub.7 - $\alpha$ -olefin chain transfer agent, and a diluent amount of C.sub.4 -C.sub.8 -cycloalkane with an organoammonium molybdate, metal halide or metal oxyhalide catalyst in combination with an organoaluminum (or organolin) halide co-catalyst present in an amount in which 1 mol of ROMP catalyst forms from 1500 mols to 30,000 mols, preferably from 2000 to 10,000 mols of polymer; maintaining the first reaction zone substantially free from back-mixing with copolymer from a succeeding reaction zone maintained at a temperature at least 20° C. higher than that in the first reaction zone; maintaining the last reaction zone at a temperature in the range from 120° C.-140° C.; continuously controlling the temperature in the last reaction zone by varying only the rate of addition of a combination of catalyst and C.sub.3 -C.sub.7 alkene chain transfer agent; and, continuously crosslinking a major molar proportion of all symmetrical trimer present to produce from 0.1% to 2% by weight of gel/100 parts of copolymer; whereby a copolymer having a mol wt M.sub.w >35,000, preferably in the range from 50,000 to 200,000, with M.sub.w /M.sub.n <5 and a T.sub.g in the range from 135° C.-200° C. is produced in less than 10 min residence time through the reactor.

DETD The process of this invention comprises the ring-opening polymerization of cyclic olefins that are characterized by the presence of at least one norbornene moiety having the general structures shown below: ##STR2## These cyclic olefins may be either substituted or unsubstituted and can exist either in the endo- or exo- form, but are generally present as a mixture of both forms. When polymerized in a ROMP reaction, the polymer formed may have either cis- or trans- unsaturation in the backbone. Suitable cyclic olefins include substituted and unsubstituted norbornenes, dicyclopentadienes, dihydrodicyclopentadienes, trimer of cyclopentadiene, tetracyclododecenes, ethylidene-TDs, hexacycloheptadecenes, ethylidenyl norbornenes and vinyl norbornenes.

CLM What is claimed is:

1. A process for polymerizing a substantially anhydrous solution in which a processable ring-opened polymer is formed by ring opening metathesis polymerization in at least a first and a last reaction zone of a multi-zoned, single-stage, reaction vessel, said solution including at least one multi-ringed monoolefinically unsaturated cycloolefin monomer selected from the group consisting of bicyclo[2.2.1]hept-2-ene ("norbornene" "NB") and substituted embodiments thereof, comprising, (a) continuously introducing said monomer into said first reaction zone in combination with (i) a diluent amount of a C.sub.4 -C.sub.8 -cycloalkane, and (ii) a minor molar amount, relative to the moles of said monomer, of a lower C.sub.3 -C.sub.7 alkene chain transfer agent present in a predetermined amount correlatable with a desired weight average molecular weight Mw in the range from about 30,000 to about 500,000 of said polymer, and (iii) a catalyst system consisting essentially of a catalyst selected from the group consisting of organoammoniummolybdate, Mo(Cl).sub.5, W(Cl).sub.6, WO(Cl).sub.4, WO(OR).sub.4-x Cl.sub.x where R represents alkyl, phenyl, phenyl substituted phenyl, phenylalkyl, and halogen substituted derivatives of alkyl, phenyl, and phenyl substituted phenyl and phenylalkyl; x is an integer in the range from 0 to 4; in combination with an organoaluminumhalide co-catalyst, present in an amount effective to produce said polymer, said co-catalyst being represented by R'.sub.y